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Polyimides from cyclobutane dianhydrides have been prepared and have been shown to be sensitive to electron beams as well as to deep UV irradiation. Synthesis, thermal properties and sensitivity data are presented.

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ELECTRON-BEAM POSITIVE POLYIMIDES

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ABSTRACT

Polyimides from cyclobutane dianhydrides have been prepared and have been shown to be sensitive to electron beams as well as to deep UV irradiation. Synthesis, thermal properties and sensitivity data are presented.

1. INTRODUCTION

We have been studying the synthesis of an intrinsically photosensitive polyimide for use in integrated circuit (IC) technology. In the fabrication of multilevel metal-insulator IC structures, Kapton polyimide has proven to be a good insulator between metalization layers because of its thermal stability, chemical resistance, and dielectric properties. The intermediate polyamic acid formed is soluble and can be spun to films that can be cured to insoluble polyimide structures. Once the material is cured, it is generally insoluble and infusible and is extremely thermally stable.

The insolubility and infusibility of Kapton require that patterning of polyimide layers be accomplished indirectly by photoresist technology. This process entails the spinning and curing of the polyimide layer, formation of a polysulfone lift-off layer, and deposition of a SiO_2 masking layer followed by a top layer of resist coating. The pattern is defined by electron beam or optical lithography, the underlying layers are etched with reactive ion etching, metal is deposited, and the polysulfone and excess metal are "lifted off" with solvent. If the polyimide layer itself could be made to be intrinsically photosensitive, it is obvious that the process of image generation could be greatly simplified. Several photonegative polyimide precursor systems have been developed. In the most common type, the intermediate polyamic acid is partially esterified with photocross-linkable alcohols (1). Irradiation of these esters causes them to become insoluble and

enables them to be used to form negative images upon treatment with solvent. After imaging, the films are thermally converted to polyimide that is photoinsensitive. A photopositive system is much more desirable because of the swelling attendant upon solvent development of negative images. A photopositive polyimide containing photosensitive sulfonium salt units has recently been described (2). We have reported the use of 1,2:3,4-cyclobutanedianhydride to form a polyimide which can be imaged by deep UV irradiation at a wavelength which corresponds to energy absorption by the cyclobutane imide moiety (3a,b). This polymer has been described for use as a colorless polyimide (4,5) and similar polyimides have been prepared by solution polymerization of aliphatic bis-maleimides (6,7).

We now wish to report the electron-beam sensitivity of these two polyimides.

2. EXPERIMENTAL

Dimethylacetamide (DMAC) was dried over calcium hydride and distilled at reduced pressure.

2.1 Dimerization of Maleic Anhydride

A solution of maleic anhydride in carbon tetrachloride was irradiated with an unfiltered 450 Watt Hanovia high pressure

mercury arc for 1 hour to form 1,2,3,4 cyclobutanetetracarboxylic 1,2:3,4-dianhydride (CBDA) (8). CBDA precipitated from solution and was collected by filtration. CBDA was purified by successive recrystallizations from acetic anhydride (until the filtrate was colorless) to give a white solid which does not melt up to 300°C (eq 1).

2.2 Polymerization

To a dry, three-necked, 100-mL round-bottomed flask fitted with a mechanical stirrer, nitrogen inlet, and condenser were added 0.64031 (3.1977 mmol) of oxydianiline (Aldrich Gold Label), dry DMAC (60 mL) and 0.62714g (3.1977 mmol) of CBDA. The reaction was allowed to proceed at room temperature under dry nitrogen for 18.5 hours. The resulting polyamic acid was precipitated twice into methanol and dried in vacuo at room temperature for 24 hours (eq 2).

The intrinsic viscosity of the resulting polyamic acid was 1.47 dL/g measured with an Ubbelohde viscometer at 25.00°C in DMAC.

The polyamic acid was cured to the polyimide by heating films cast by solvent evaporation in a watch glass, in an oven under nitrogen for 2 hours at 100°C, 2 hours at 175°C, and 2 hours at 250°C. The resulting polyimide films were colorless (eq 3).

2.3 Dimerization of Citraconic Anhydride

A solution of citraconic anhydride and 7-wt% of benzophenone in freshly distilled dioxane was irradiated with an unfiltered 450 Watt Hanovia high pressure mercury arc for 18 hours to form 1,3-dimethyl-1,2,3,4-cyclobutanetetracarboxylic 1,2:3,4-dianhydride (DMCBDA) (9). The stereochemistry of the product has been shown to be *cis, anti, cis* by distinguishing between head-to-head and head-to-tail dimerization from examination of the C^{13} -H nmr spectr (10). DMCBDA precipitated from solution, was collected by filtration and was purified by repeated recrystallizations from ethyl acetate-hexanes to give a white solid which does not melt up to 300°C (eq 4).

2.4 Polymerization

To a dry, three-necked, 100-mL round-bottomed flask fitted with a magnetic stirrer, nitrogen inlet and condenser were added 1.17313g (5.2332 mmol) of DMCBDA, dry DMAC (50 mL) and 1.04790g (5.2332 mmol) of oxydianiline (Aldrich Gold Label). The reaction was allowed to proceed at room temperature under nitrogen for 17 hours, the temperature was then raised to 70°C and the reaction continued for an additional 20 hours. The resulting polyamic acid was precipi-

tated into methanol and dried in vacuo at room temperature for 24 hours (eq 5).

The polyamic acid was cured to the polyimide by heating films cast by solvent evaporation in a watch glass, in an oven under nitrogen for 2 hours at 75°C, 2 hours at 150°C, and 2 hours at 200°C (eq 6).

2.5 Wafer Preparation and Exposure

Silicon wafers were spin-coated with 7% solutions of the polyamic acids. The polyamic acid was then thermally converted to polyimide according to the appropriate heating cycle and film thicknesses (0.6-1.3 microns) were measured with a Dektak Profilometer.

The polyimide films were exposed by an IBM EL-2 Lithography system at incident doses ranging from 56-800 μ Coulombs/cm². The samples for dissolution rate studies were irradiated by flood exposures.

Development was carried out by immersing the samples in an appropriate solvent for 30 seconds and then immersing the samples in deionized water for 15 seconds. After development the samples were baked at 120°C for 30 minutes.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show differential scanning calorimograms

under nitrogen, of the polyamic acids. From these scans it is apparent that conversion of polyamic acid to polyimide takes place in the range of 150-250°C. Subsequent rescanning of the sample shows no transitions in this region.

Figures 3 and 4 show the thermogravimetric behavior, under nitrogen, of the polyamic acids. The weight loss corresponding to the curing of the polyamic acid to the polyimide structure can be seen and one also sees that, once the polyimide is formed, 50% weight loss occurs at about 450°C and after heating the sample to 1200°C there is a residual weight of approximately 28%.

Table 1 compares the deep UV sensitivity of the two polyimides. The results clearly indicate that the presence of two methyl groups on the cyclobutane ring in the polyimide facilitates the cleavage of the backbone, perhaps because steric compression favors the reverse reaction. In addition, the added methyl groups causes the polyimide to be soluble presumably by hindering intermolecular association. This polyimide is soluble in polar aprotic solvents such as DMSO, DMF, DMAC, and NMP.

Figure 5 shows the electron beam sensitivity curves for the polyimides. After exposure, the polyimide derived from CBDA was developed with DMAC and

the polyimide derived from DMCBDA was developed with ethyl acetate, washed, and dried, and the remaining thickness was measured with a Dektak Profilometer. In Figure 5, doses up to 800 $\mu\text{Coulombs/cm}^2$ remove approximately 40% of the polyimide derived from CBDA and up to 70% of the polyimide derived from DMCBDA. Although we have clearly shown that these materials undergo a retrocyclization upon irradiation with ultraviolet light (3a,b) it is not readily apparent, a priori, that these materials should be sensitive to electron beam-induced processes. The photochemical process occurs selectively from an excited state of the chromophore which is populated either directly or by sensitization via energy transduction by the aromatic residues of the polymer. Electron beam processes are much more energetic and indiscriminate in causing degradative processes which, if they solubilize a polymer, do so by causing random chain scissions.

The first indication that these materials were sensitive to electron irradiation was given when electron impact mass spectrometry indicated that a model compound prepared by reacting CBDA with p-anisidine (eq 7) cleaved to give a fragment which had an m/e value (203) which corresponds to 1/2 the mass of the starting material (eq 8).

Figures 6 and 7 are examples of nonoptimized positive images generated from CBDA polyimide.

4. CONCLUSION

We have successfully prepared polyimides which are not only sensitive to UV irradiation but which are also e-beam sensitive and have demonstrated the utility of this system for image generation. Work is continuing to extend the limits of sensitivity, to optimize image dimensions and to explore structure-sensitivity relationships of the class of polyimides derived from cyclobutane dianhydrides and diamines as well as to explicate the mechanistic underpinnings of this process.

5. ACKNOWLEDGMENT

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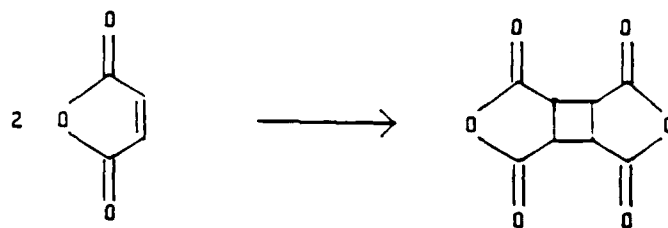
7. BIOGRAPHY

James A. Moore obtained a B. S. degree from St. John's University, and a Ph. D. degree from the Polytechnic Institute of Brooklyn in 1967. Thereafter he was a National Institutes of Health Postdoctoral Fellow at the University of Mainz, West Germany, and a Research Associate at the University of Michigan in 1968. In 1969 he joined the faculty of the Chemistry Department of Rensselaer Polytechnic Institute where he is Full Professor of Organic and Polymer Chemistry. He is a member of the American Chemical Society, the Editorial Boards of *Macromol-*

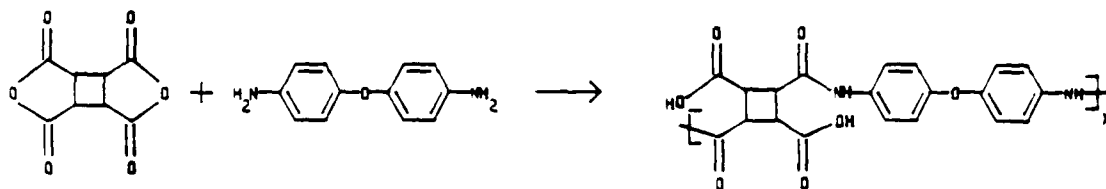
ecular Syntheses and *Chemistry of Materials* and is Associate Editor of *Organic Preparations and Procedures, International*. Dr. Moore has more than 130 publications, including 6 books, and in 1985 was awarded the American Cyanamid Award for Significant Achievement in Synthesis.

Andrew N. Dasheff obtained a B. A. degree from Franklin and Marshall College in 1984, and a M. S. degree from Rensselaer Polytechnic Institute in 1988. Mr. Dasheff is currently a graduate student at RPI where he expects to receive his Ph. D. degree in September 1989. Mr. Dasheff is a member of the American Chemical Society. In 1988, he was awarded a Goodyear Fellowship.

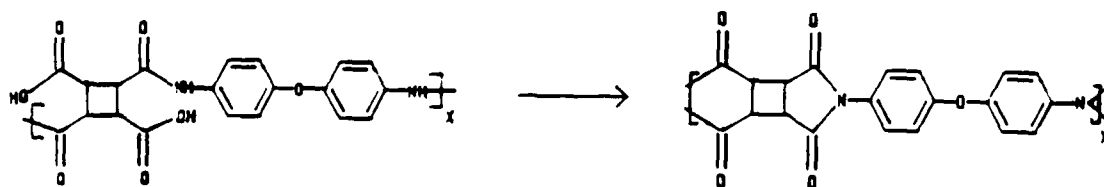
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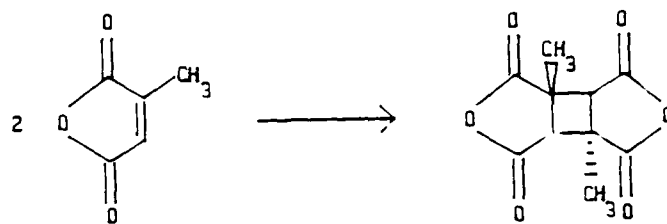
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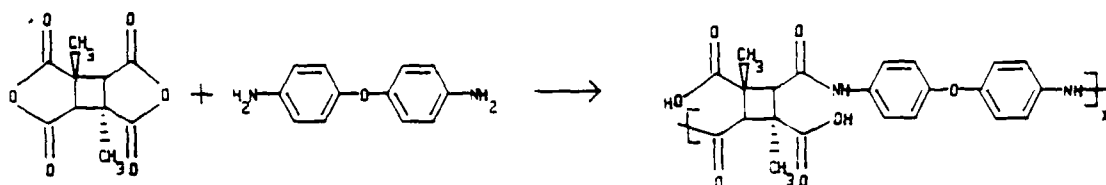
Equation 3



Equation 4



Equation 5



Equation 6

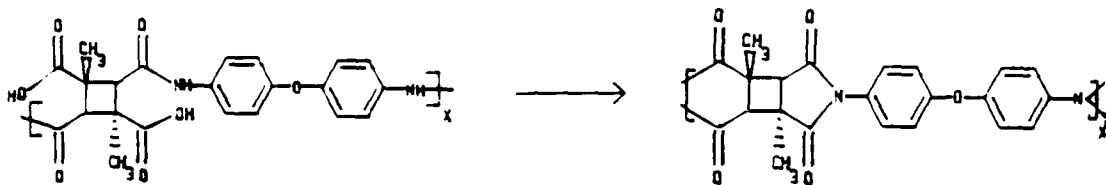


Figure 1. Differential scanning calorimogram of CBDA polyamic acid.

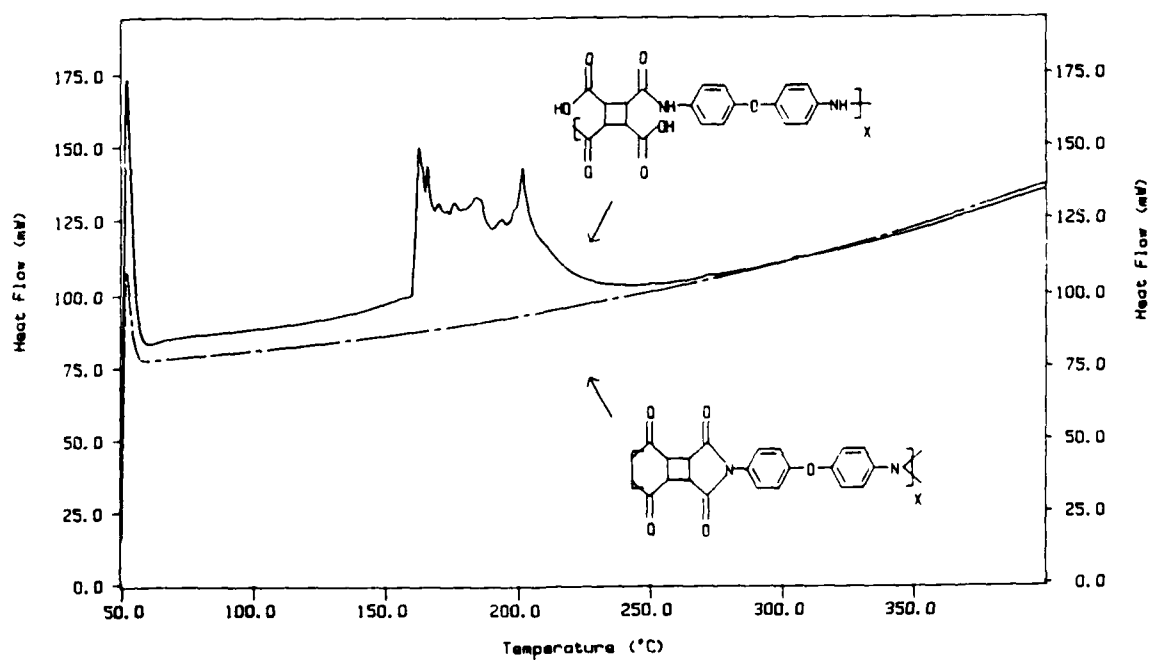
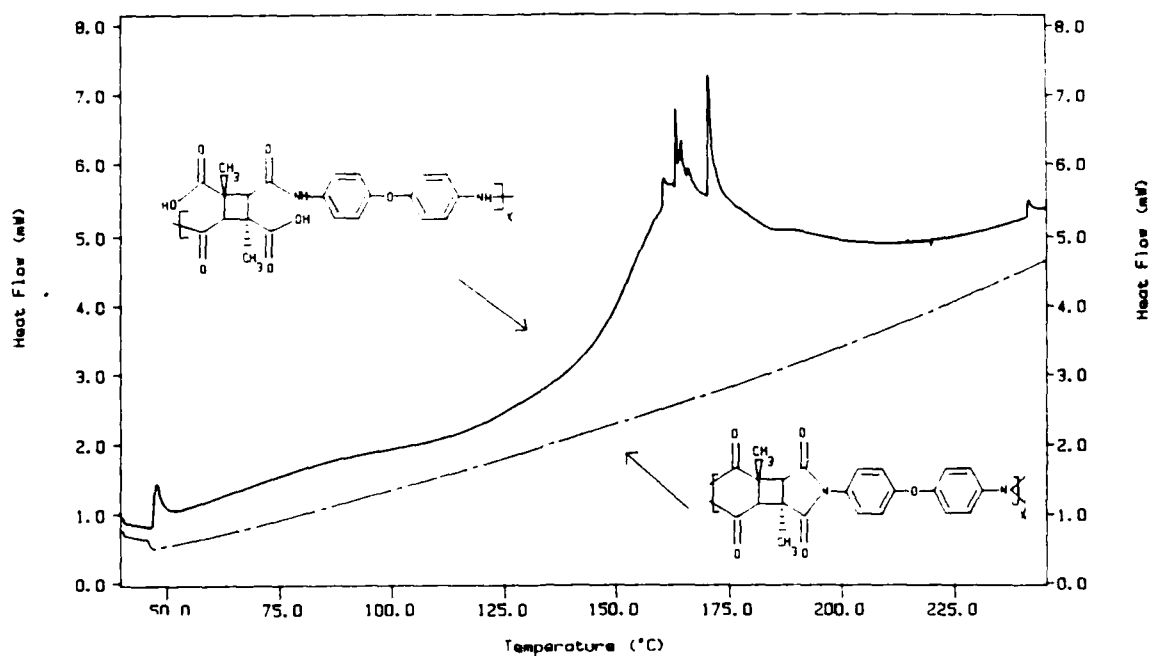


Figure 2. Differential scanning calorimogram of DMCBDA polyamic acid.



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Figure 3. Thermogravimetric analysis of CBDA polyamic acid.

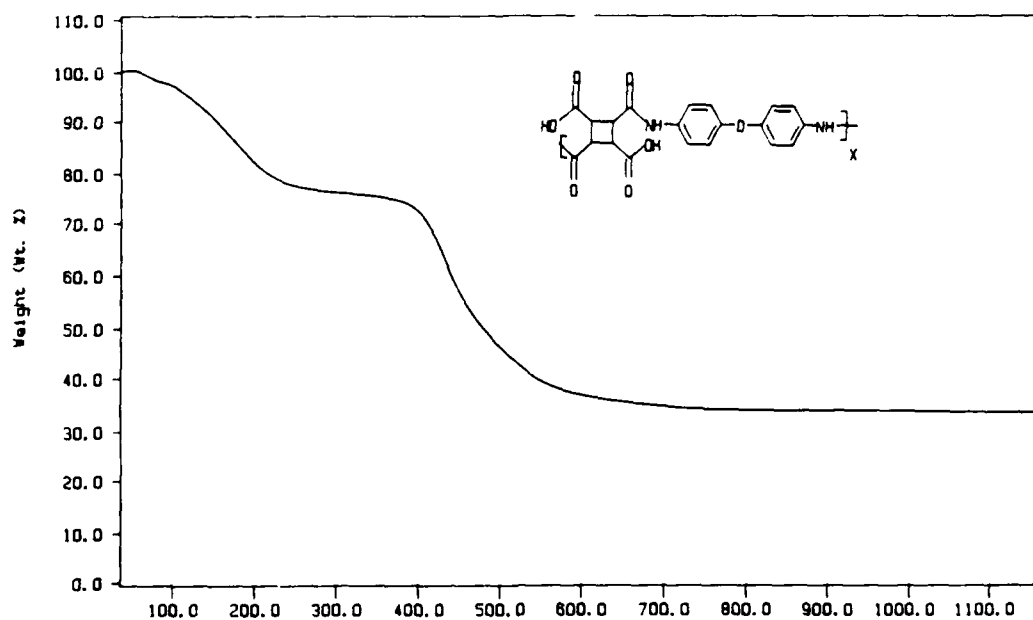
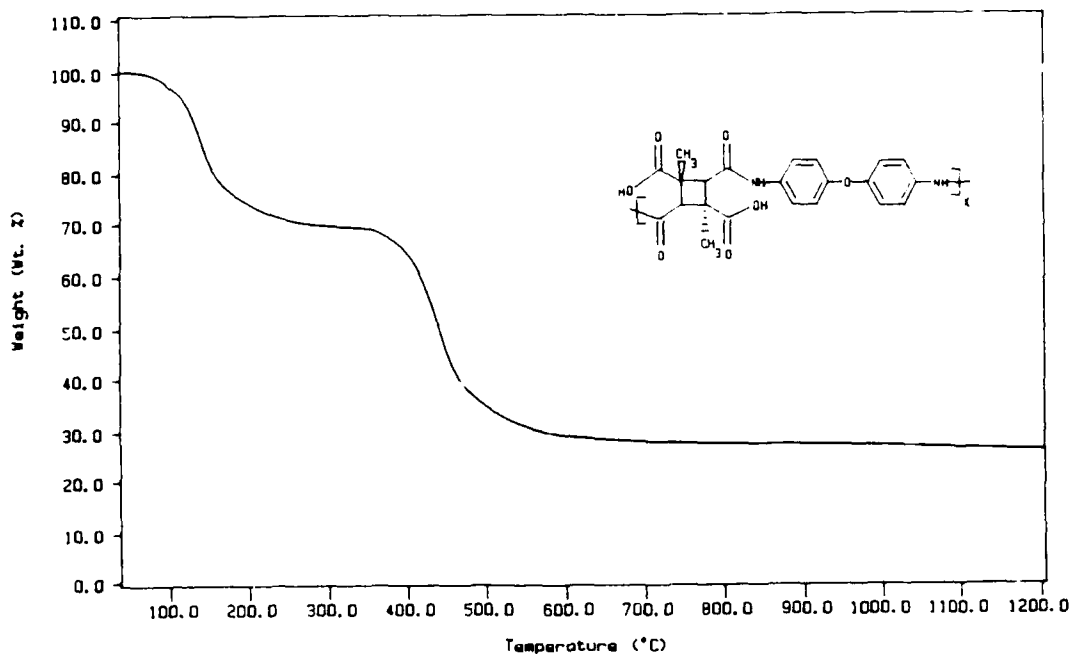


Figure 4. Thermogravimetric analysis of DMCBDA polyamic acid.



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Table 1. UV sensitivity of two cyclobutane-containing polyimides.

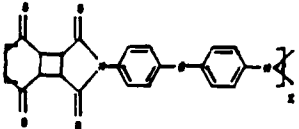
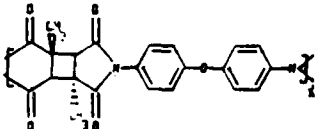
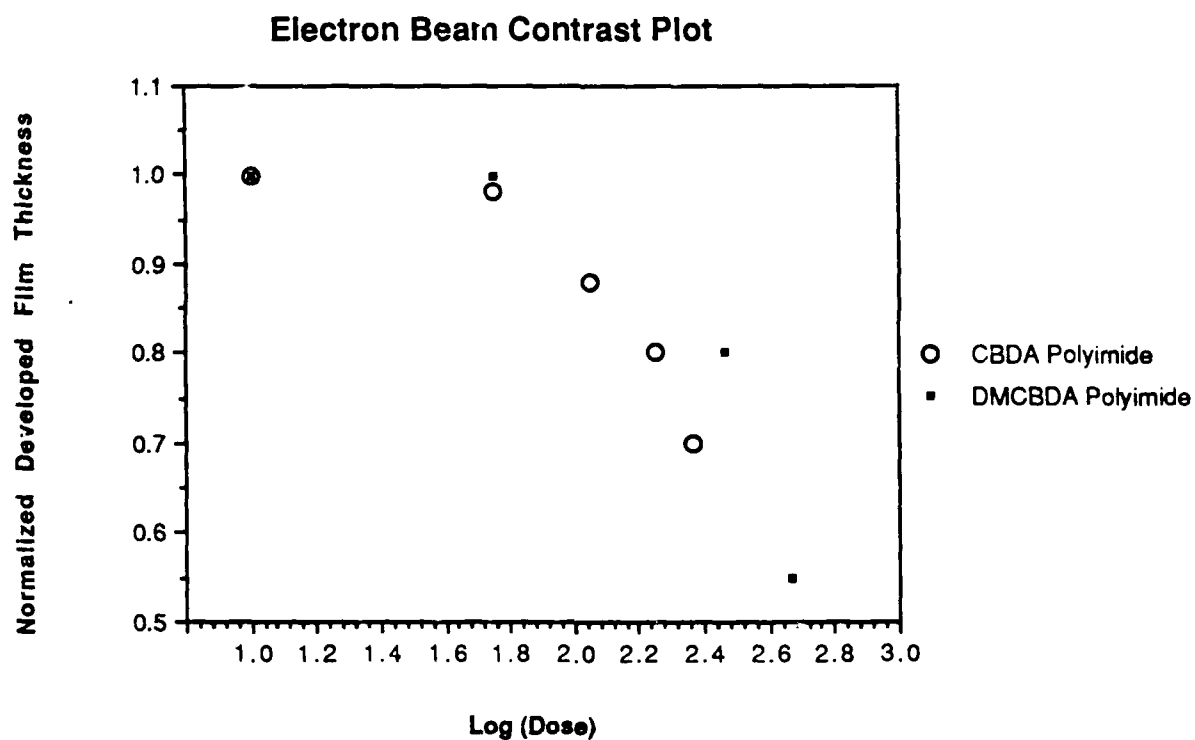
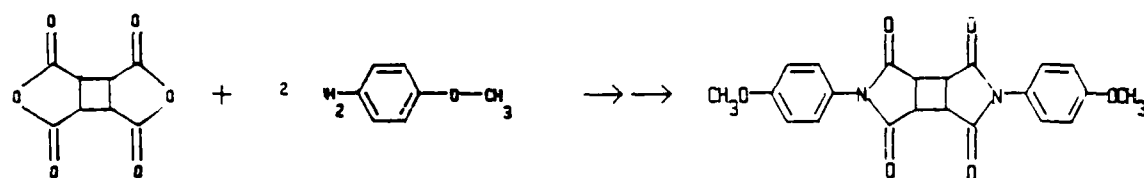
		
DOSE (mJ/sq. cm.)	% Film Remaining	% Film Remaining
0	100	100
100	79.4	33.3
200	76.6	30.0
300	76.9	28.3
400	76.6	23.3
500	75.4	21.7

Figure 5. Electron beam contrast curve of polyimides.



Equation 7



Equation 8

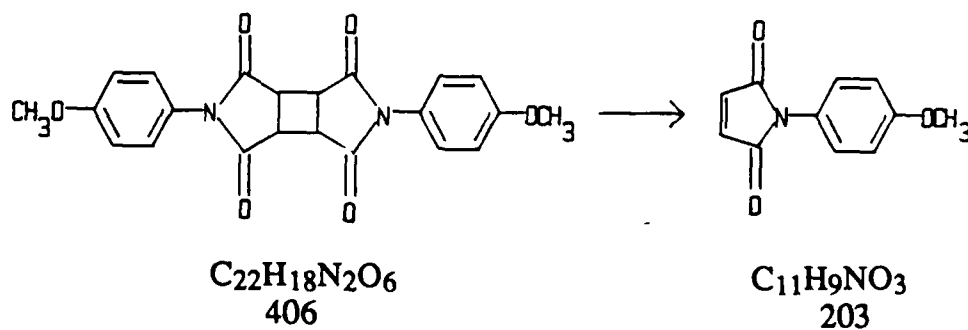


Figure 6. Ultraviolet generated images 2-, 4-, 6- μm lines at dose of 2.5 J/cm² (DMAC; developed for 30 s) in CBDA polyimide.

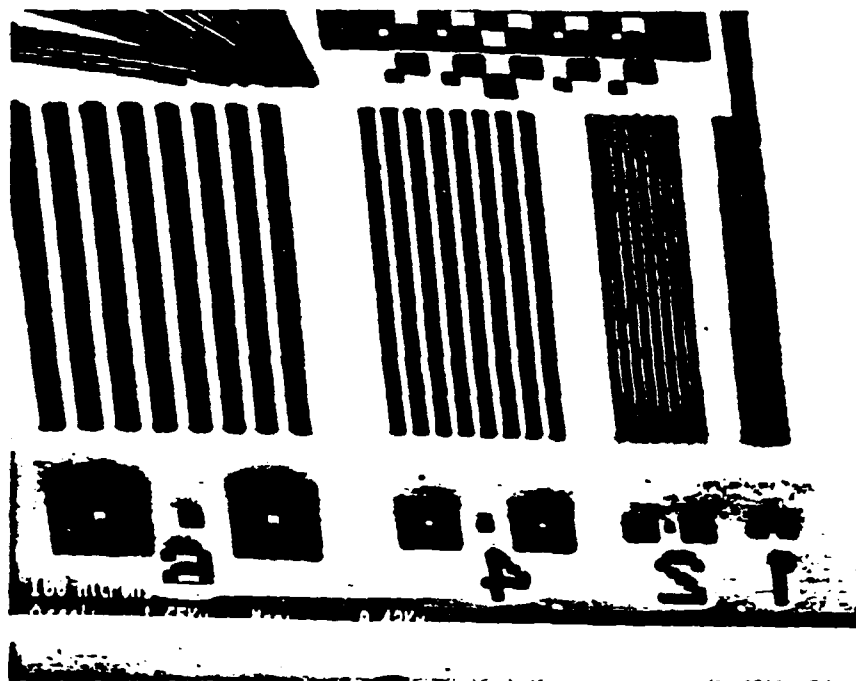
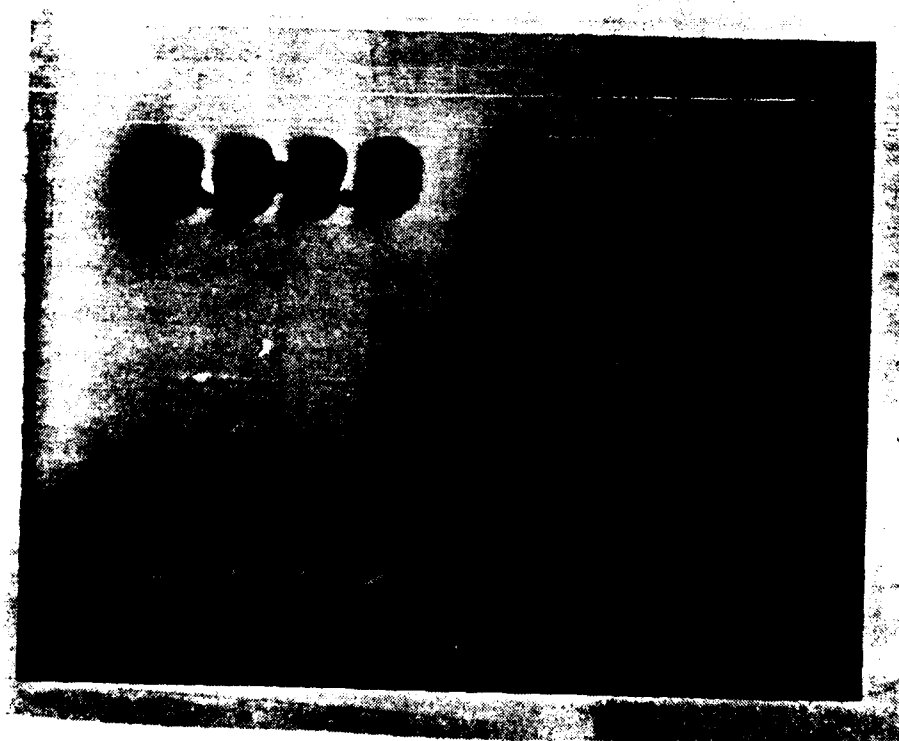


Figure 7. Electron beam generated images 0.5 μm lines at dose of 500 $\mu\text{Coulombs/cm}^2$ (DMAC; developed for 30 s) in CBDA polyimide.



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